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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of polyorganosiloxane particles, and the manufacturing method of a silica particle. It is still more detailed particle diameter (about 4-10 micrometers) with this invention preferred as the spacer for liquid crystal displays, standard particles, etc., And the polyorganosiloxane particles of mono dispersion [particle size distribution] so that the thing of desired particle diameter may be obtained, Baking treatment of the method which yield is good in a short time, and it moreover is not restricted to the specific gravity of a raw material, but is manufactured, and the polyorganosiloxane particles obtained by this method is carried out, and it is related with the method of manufacturing a silica particle suitable as the spacer for liquid crystal displays, standard particles, etc.

[0002]

[Description of the Prior Art]Although it is known conventionally that a monodisperse silica particle (it may only be hereafter called a monodisperse silica particle) has useful particle size distribution as various fillers, a ceramics raw material, etc., these days, the use as a spacer of a liquid crystal display especially attracts attention, and it is beginning to be used.

[0003]The particles of a glass fiber chip or a synthetic resin have been conventionally used for the spacer of a liquid crystal display. Although the glass fiber chip is excellent in the diameter accuracy of a fiber, dispersion is large to the length, and a too much long thing is viewed, has a possibility of falling, for image quality, and it However, since the end is sharp, There is a possibility of damaging the orienting film fabricated on the substrate, a protective film, a light filter, or an electric element. Since particle size accuracy is inferior, the particles of a synthetic resin cannot fill the performance demanded as a spacer for liquid crystal displays. Therefore, when more advanced gap accuracy is required, particle size accuracy is good and a thing

without a possibility of damaging electric elements formed on the substrate in the globular form, such as an orienting film, a protective film, a light filter or an ITO conducting film, is required.

[0004]As what fills these demands, the silica particle obtained hydrolysis and by carrying out a polycondensation in the silicon alkoxide is proposed. This silica particle has high (1) purity, and (2) particle size accuracy with little influence on the liquid crystal by a leached moiety is good, (3) which can make the CV value (coefficient of variation) acquired by lower type valve flow coefficient(%) = [the standard deviation (micrometer) of the diameter of a particle] / [mean-particle-diameter (micrometer)] x100 10% or less, since it can be made an almost perfect real ball, It has an advantage, like there is no possibility of damaging electric elements etc. which were formed on the substrate, such as an orienting film, a protective film, a light filter or an ITO conducting film.

[0005]Since the silica particle obtained by hydrolysis and the polycondensation of the silicon alkoxide has the above advantages, many manufacturing methods are proposed until now. As a manufacturing method of spherical polymethylsilsequioxane, for example, methyl trialkoxysilane and its partial hydrolysis condensate, The method of making it react, holding a two-layer state is proposed, without mixing on parenchyma the partially aromatic solvent solution of the solution or the water, and the organic solvent containing ammonia and amine (JP,4-70335,B).

[0006]However, in this method, although the particle diameter of the polymethylsilsequioxane particles to generate is controlled by ammonia in the lower layer at the time of preparation, or concentration of amine, There is a problem that the path of the particles obtained eventually does not turn into the target particle diameter even if it is easy to produce variation in a generating particle nuclear number and reacts on reaction-of-identity conditions, since generation of a nuclear particle is indefinite. For example, when manufacture is performed 10 times on the same conditions in order to obtain the particles whose mean particle diameter is 5 micrometers, about (about **2.0 micrometers) 40% of variation arises to the target particle diameter.

[0007]Thus, if desired particle diameter is not obtained, the problem of being hard to use it for the spacer for liquid crystal displays as which the particle size accuracy is required strictly will arise. In particular, in these days, obtaining the polyorganosiloxane particles of particle diameter (about 4-10 micrometers) suitable as a spacer use for liquid crystal displays with sufficient particle size accuracy is called for.

[0008]This invention persons are the bases of such a situation, and have particle diameter (about 4-10 micrometers) suitable as a spacer for liquid crystal displays especially, and the polyorganosiloxane particles of mono dispersion [particle size distribution] so that the thing of desired particle diameter may be obtained, Repeat research about the method of

manufacturing efficiently, and previously the silicon compound which the non-hydrolytic basis and the alkoxyl group of hydrolysis nature combined with the silicon atom, When carrying out hydrolysis condensation in the aqueous solution of ammonia or amine, a hydrolysis reaction by specific initial pH. And after having carried out until it reached a value with the degree of fall of pH, and making seed particles generate, this was diluted and the method of performing operation of, adding the above-mentioned silicon compound subsequently to this diluent, and growing up seed particles, once or more was found out (Japanese Patent Application No. No. 268084 [ten to]).

[0009]According to this method, compared with the method of given [aforementioned] in JP,4-70335,B, particle size accuracy improves substantially and with comparatively big particle diameter (about 4-10 micrometers). And the polyorganosiloxane particles of mono dispersion [particle size distribution] can be manufactured so that the thing of desired particle diameter can obtain with sufficient accuracy. However, although this method was a desirable method, about the time required for manufacturing desired polyorganosiloxane, yield, and the selection flexibility of the raw material, the room of improvement was left behind industrially.

[0010]The method of manufacturing a real ball-like silica particle is indicated by on the other hand calcinating polymethylsilsesquioxane powder at the temperature (500-1300 **) which the organic group (methyl group) which it has in the intramolecular decomposes (JP,5-13089,B). In this method, since the methyl trialkoxysilane used as a raw material has high reactivity, it can large-diameter-be easy toize by a single step, and can obtain the target silica particle for a short time. However, if big particle diameter, for example, a not less than 3-micrometer particle, is made to form suddenly by a single step, When variation surely arose in the particle diameter of particles, and a CV value became high and also polymethyl siloxane particles were calcinated and silica-ized, contraction of particle diameter was remarkable and there were problems, like it is difficult to obtain the last particle diameter of the silica particle made into the purpose with sufficient accuracy, and there is. Therefore, the silica particle obtained by this method was unsuitable for the use of the spacer of the liquid crystal display in which high particle size accuracy [Bure (particle diameter of the purpose particles - particle diameter of the obtained particles) of a low CV value and low particle diameter] is demanded especially, etc.

[0011]

[Problem(s) to be Solved by the Invention]Under such circumstances, the 1st purpose of this invention, It is in providing the method of being particle diameter (about 4-10 micrometers) suitable as the spacer for liquid crystal displays, standard particles, etc., and yield being good in a short time, and it not being restricted to the specific gravity of a raw material moreover, but manufacturing the polyorganosiloxane particles of mono dispersion [particle size distribution] so that the thing of desired particle diameter may be obtained. In the method of the 2nd purpose of this invention calcinating polyorganosiloxane particles, and manufacturing a silica

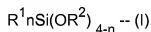
particle, It is in the thing which manufacture the silica particle of high particle size accuracy [Bure (particle diameter of the purpose particles - particle diameter of the obtained particles) of a low CV value and low particle diameter] by simple operation for a short time and for which an advantageous manufacturing method is provided industrially.

[0012]

[Means for Solving the Problem]In order that this invention persons may attain said purpose, as a result of repeating research wholeheartedly, a silicon compound which a non-hydrolytic basis and an alkoxyl group of hydrolysis nature combined with a silicon atom is used as a uniform aqueous solution, After making it hydrolyze and condense and preparing seed particle liquid, it found out that the 1st purpose could be attained by an aqueous solution of the above-mentioned silicon compound performing dilution operation, and growing up this particle based on dilution magnification called for according to a specific expression of relations.

[0013]Polyorganosiloxane particles are heat-treated, if temperature up is promptly carried out to temperature more than decomposition temperature of this organic group when decomposing an organic group contained in it, decomposition of this organic group and desorption take place rapidly, disruptive strength of particles may fall or particles may break. In order to solve such a problem, after this invention persons repeated research further and did preliminary calcination at a specific temperature, by carrying out actual calcination at temperature more than decomposition temperature of this organic group, they could solve the above-mentioned problem and found out that the 2nd purpose could be attained.

[0014]This invention is completed based on this knowledge. That is, this invention is (1) general-formula (I).



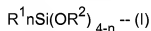
R^1 is a non-hydrolytic basis among a formula -- an alkyl group of the carbon numbers 1-20. An alkyl group of the carbon numbers 1-20 which have a (meth)acryloyloxy group or an epoxy group, An alkenyl group of the carbon numbers 2-20, an aryl group of the carbon numbers 6-20, or an aralkyl group of the carbon numbers 7-20, R^2 shows an alkyl group of the carbon numbers 1-6, and n shows an integer of 1-3, When there is two or more R^1 , R^1 each may be mutually the same, or may differ, When there is two or more OR^2 , each OR^2 may be mutually the same or may differ. A silicon compound expressed is used as a uniform aqueous solution, Make it hydrolyze and condense under catalyst existence, and polyorganosiloxane particles are formed, Obtained polyorganosiloxane particle liquid is used as seed particle liquid, this is diluted with an aqueous solution of the above-mentioned silicon compound, growth operation is performed, the mean particle diameter \bar{r} (micrometer) is measured after seed particle formation in a manufacturing method of polyorganosiloxane particles into which particle diameter is grown up, and it is expression-of-relations (II).

$$R = r_x (K \times C \times M / m + 1)^{1/3} \quad \text{-- (II)}$$

A constant as which determine r_x , however R with the purpose last particle diameter (micrometer), K is determined by dilution magnification (preset value) of seed particle liquid, and C is determined by growth reaction conditions of seed particles, and M and m are the concentration (mass %) of a silicon compound used in a particle growth process and a seed particle formation process, respectively. Dilution operation is performed based on dilution magnification determined according to the purpose last particle diameter according to), After starting a growth reaction, particle diameter is measured every [continuously or] fixed time, manufacturing method of polyorganosiloxane particles stopping a reaction when change of this particle diameter is lost on parenchyma . And above a temperature lower 100 °C than decomposition temperature of an organic group contained in it in polyorganosiloxane particles obtained with (2) described methods, And after carrying out reserve baking treatment at temperature of the range of less than decomposition temperature of the organic group concerned, a manufacturing method of a silica particle carrying out baking treatment at temperature more than decomposition temperature of the organic group concerned is provided.

[0015]

[Embodiment of the Invention]First, the manufacturing method of the polyorganosiloxane particles of this invention is explained. In the method of this invention, it is general formula (I) as a raw material.



It comes out and the silicon compound expressed is used.

[0016]In the above-mentioned general formula (I), R^1 shows the alkyl group of the carbon numbers 1-20 which have the alkyl group, (meth)acryloyloxy group, or epoxy group of the carbon numbers 1-20, the alkenyl group of the carbon numbers 2-20, the aryl group of the carbon numbers 6-20, or the aralkyl group of the carbon numbers 7-20. Here, as an alkyl group of the carbon numbers 1-20, the thing of the carbon numbers 1-10 may be preferred, and this alkyl group may be straight chain shape and branched state and annular any. As an example of this alkyl group, a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, a pentyl group, a hexyl group, an octyl group, a cyclopentyl group, a cyclohexyl group, etc. are mentioned. As an alkyl group of the carbon numbers 1-20 which have a (meth)acryloyloxy group or an epoxy group, the alkyl group of the carbon numbers 1-10 which have the above-mentioned substituent may be preferred, and this alkyl group may be straight chain shape and branched state and annular any. As an example of the alkyl group which has this substituent, gamma-acryloyloxypropyl group, gamma-methacryloyl oxypropyl group, gamma-glycidoxy propyl

group, 3, and 4-epoxycyclohexyl group etc. are mentioned. As an alkenyl group of the carbon numbers 2-20, the alkenyl group of the carbon numbers 2-10 may be preferred, and this alkenyl group may be straight chain shape and branched state and annular any. As an example of this alkenyl group, a vinyl group, an allyl group, a butenyl group, a hexenyl group, an octenyl group, etc. are mentioned. As an aryl group of the carbon numbers 6-20, the thing of the carbon numbers 6-10 is preferred, for example, a phenyl group, a tolyl group, a xylyl group, a naphthyl group, etc. are mentioned. As an aralkyl group of the carbon numbers 7-20, the thing of the carbon numbers 7-10 is preferred, for example, benzyl, a phenethyl group, a phenylpropyl group, a naphthyl methyl group, etc. are mentioned.

[0017]On the other hand, R^2 may be an alkyl group of the carbon numbers 1-6, may be straight chain shape and branched state and annular any, and as the example, A methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, a pentyl group, a hexyl group, a cyclopentyl group, a cyclohexyl group, etc. are mentioned. When n is an integer of 1-3, R^1 each may be mutually the same and it may differ, when there is two or more R^1 , and there is two or more OR^2 , each OR^2 may be mutually the same and may differ.

[0018]As an example of a silicon compound expressed with said general formula (I), Methyl trimethoxysilane, methyl triethoxysilane, a methyl tripropoxy silane, A methyl triisopropoxy silane, ethyltrimethoxysilane, ethyltriethoxysilane, Propyl triethoxysilane, butyltrimethoxysilane, phenyltrimethoxysilane, Phenyltriethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, Gamma-glycidoxypropyltrimethoxysilane, gamma-acryloyloxypropyl trimethoxysilane, gamma-methacryloyl oxypropyl trimethoxysilane, dimethyldimethoxysilane, methylphenyl dimethoxysilane, etc. are mentioned. In these, especially methyl trimethoxysilane and vinyltrimethoxysilane are preferred. In this invention, one sort of silicon compounds expressed with said general formula (I) may be used as a raw material, and it may use combining two or more sorts.

[0019]The method of this invention uses as seed particle liquid the polyorganosiloxane particle liquid obtained by using said silicon compound as a uniform aqueous solution, making it hydrolyze and condense under catalyst existence, and making polyorganosiloxane particles form, and is this by the aqueous solution of the above-mentioned silicon compound

Expression-of-relations (II)

$$R = r \{ K \cdot C \cdot M / (m + 1) \}^{1/3} \quad \text{-- (II)}$$

The purpose last particle diameter (micrometer) and r [, however R The mean particle diameter of the seed particles in seed particle liquid (micrometer), The constant as which K is determined by the dilution magnification (preset value) of seed particle liquid, and C is determined by the growth reaction conditions of seed particles, and M and m are the

concentration (mass %) of the silicon compound used in a particle growth process and a seed particle formation process, respectively. According to], it dilutes based on the dilution magnification determined according to the purpose last particle diameter, and growth operation is performed, it is the method of growing up particle diameter, and the following operation is specifically included.

[0020](1) Growth of calculation (5) particle diameter and (6) reaction stop of measurement of the formation (4) seed particle diameter of the preparation (3) seed particles of the liquid for preparation (2) particle-diameter growth of the liquid for seed particle formation and the liquid for particle diameter growth of an addition (dilution magnification) [0021]Next, each above-mentioned operation is explained in detail.

(1) In the method of preparation this invention of the liquid for seed particle formation, Formation of seed particles and growth of particle diameter can be used regardless of specific gravity out of the compound expressed with said general formula (I) as a silicon compound used for preparation of this liquid for seed particle formation, choosing them suitably, in order to carry out by a homogeneous system, respectively. In carrying out formation of seed particles, and growth of particle diameter by a two-layer method, respectively, Since it is required as a silicon compound to use what has specific gravity lighter than an aqueous medium, it does not escape that the kind of raw material is restricted, but in this invention, since there are no restrictions of such specific gravity, the selection flexibility of a raw material is large.

[0022]Although it has miscibility to an aqueous medium as this silicon compound and there should just be no restriction in particular, what it is easy to dissolve in an aqueous medium especially, for example, the silicon compound which has a methoxy group, is preferred. As an aqueous medium, the mixture of water or water, and a water miscibility organic solvent can be used. Here, as an example of a water miscibility organic solvent, ketone, such as lower alcohol, such as methanol, ethanol, propanol, and butanol, and acetone, is mentioned. These may be independently mixed with water and may be mixed with water combining two or more sorts.

[0023]Preparation of this liquid for seed particle formation is performed by adding this silicon compound, usually agitating at the temperature of about 0-50 **, and considering it as a uniform aqueous solution into the above-mentioned aqueous medium. Under the present circumstances, below 20 mass % of the concentration of a silicon compound is preferred. When this concentration exceeds 20 mass %, there is a case where it becomes impossible to apply expression-of-relations (II). If concentration is too low not much, volume efficiency etc. will worsen and will become disadvantageous industrially. More desirable concentration is the range of 15 - 5 mass %.

[0024](2) Although the liquid for particle diameter growth of ***** of the liquid for particle

diameter growth is prepared completely like preparation of the liquid for seed particle formation of the above (1), In this liquid for particle diameter growth, the kind of the kind of silicon compound, its concentration, and aqueous medium may be the same as that of them of this liquid for seed particle formation, and although it may differ, the same thing is preferred from points, such as workability and description of the particles obtained.

[0025](3) Agitating the liquid for seed particle formation prepared by the formation above (1) of seed particles, add ammonia and/or an amine water content nature solution at a stretch preferably as a catalyst, make a silicon compound hydrolyze and condense, make seed particles form, and consider it as seed particle liquid. Here, as amine, monomethylamine, dimethylamine, monoethyl amine, diethylamine, ethylenediamine, etc. can be mentioned preferably, for example. Although this ammonia and amine may be used independently and it may use combining two or more sorts, there is little toxicity, removal is easy, and since it is cheap, ammonia is preferred.

[0026]As ammonia and/or an amine water content nature solution, the solution which dissolved ammonia and/or amine in the partially aromatic solvent of water or water, and a water miscibility organic solvent is mentioned. Here, the same thing as what was illustrated as an example of a water miscibility organic solvent in the explanation about preparation of the liquid for seed particle formation of the above (1) can be mentioned.

[0027]As for the addition of this ammonia and/or an amine water content nature solution, it is advantageous to select so that the pH of the seed particle liquid after seed particle formation may become the range of 8.2-11.0 preferably. Although reaction temperature is influenced by the kind of silicon compound of a raw material, etc., it is generally chosen in 0-50 °C. The formation time of seed particles is usually enough in less than 1 hour. If the method by a homogeneous system is adopted like this invention, seed particles can be made to require about 4 to 10 hours, in forming seed particles by a two-layer method, but to form far for a short time.

[0028](4) Measurement of seed particle diameter and some seed particle liquid of the addition (dilution magnification) of the liquid for particle diameter growth calculatively obtained in the account (3) are extracted, After making a protective colloid formation agent contact and making protective colloid form in seed particles, the mean particle diameter (micrometer) of this seed particle is measured with a Coulter counter. Thus, it becomes measurable [without the seed particle diameter at the time of Coulter counter measurement contracting by making protective colloid form / stable].

[0029]As a protective colloid formation agent, here, for example Alkylaryl sulfonates, such as alkyl benzene sodium sulfonate, Polymer surfactants, such as anionic surface-active agents, such as fatty acid soap, such as alkyl-sulfonic-acid salts, such as sodium dodecyl sulfonate, and sodium laurate, polymethacrylic acid, alginate, polymer lactic acid, and polyvinyl

alcohol, etc. can be mentioned. In these, especially polyvinyl alcohol is preferred. These protective colloid formation agents may use one sort independently, and may use it combining two or more sorts.

[0030]Next, formula (III) which sets up the purpose last particle diameter (micrometer) and develops the above-mentioned expression-of-relations (II) for the mean particle diameter of seed particles and this purpose last particle diameter which were measured as mentioned above with the dilution magnification K

[0031]

[Equation 1]

$$\text{稀释倍率 } K = \frac{\{ (R^3 - r^3) / r^3 \} \times (m/M) - A}{B} \quad \dots \quad (III)$$

[0032](however, A and B are constants decided by the growth reaction conditions of seed particles.) -- it substitutes and the dilution magnification K is computed.

[0033]It can ask for A and B in the above-mentioned formula (III) as follows. After adding in liquid for particle diameter growth of the above (2) so that according to predetermined dilution magnification, seed particle liquid obtained above (3) with an optical microscope video micrometer. Or when particle diameter is measured every fixed time and change of particle diameter is lost on parenchyma, it ripens by adding ammonia and/or an amine water content nature solution to this, and mean particle diameter is measured, for example with a Coulter counter. changing dilution magnification for this operation -- a multiple-times deed -- the correction factor C is calculated, respectively.

[0034]From the above-mentioned result to formula (IV)

$$C = A/K + B \quad \dots \quad (IV)$$

(however, K is dilution magnification.) -- it asks for the constants A and B with which it is made satisfied.

[0035](5) Agitating liquid for particle diameter growth of the growth above (2) of particle diameter, add seed particle liquid obtained above (3) to this so that it may become the dilution magnification computed above (4), and grow up particle diameter into it. Although reaction temperature in this case is influenced by kind of silicon compound of a raw material, etc., it is generally chosen in 0-50 **.

[0036](6) After addition of seed particle liquid in the stop above (5) of a reaction, with an optical microscope video micrometer, or when particle diameter is measured every fixed time and change of this particle diameter is lost on parenchyma, ripe by adding ammonia and/or an amine water content nature solution to this. At temperature of the range of 0-50 **, this aging is usually performed for about 6 to 24 hours, although based also on a kind of silicon compound of a raw material.

[0037]Generally in this invention, growth of particle diameter of the above (5) is enough in less

than 3 hours. When adopting a two-layer method and growing up particle diameter, about 6 to 10 hours is usually required, but particle diameter can be far grown up by carrying out by a homogeneous system like this invention for a short time. In the case of a two-layer method, with moisture in the air, etc., the upper silicon compound starts self-condensation and deteriorates, for example, it becomes candy-like, coils around an impeller, the amount of silicon compounds used for growth of particle diameter falls, and particles which have desired particle diameter may not be obtained. On the other hand, in a method of this invention, since particle diameter is grown up by a homogeneous system, such a problem is not produced. [0038]In this invention, after an end of operation of the above (6), after fully washing particles generated in accordance with a conventional method, if necessary, classifying processing will be performed, a large drop child or the minimum particles are removed very much, and a drying process is performed. Although there is no restriction in particular as the classifying processing method, the wet-classification method for performing a classification using sedimentation velocity changing with particle diameter is preferred. A drying process is usually performed at temperature of the range of 100-200 **. In this invention, condensation of particles does not arise on parenchyma in this drying process.

[0039]Thus, polyorganosiloxane particles extremely approximated to the purpose last particle diameter are obtained with high yield compared with a two-layer method. 3-15 micrometers of mean particle diameter are usually 4-10 micrometers preferably, and a coefficient of variation (CV value) of particle size distribution is usually 2.5% or less, and polyorganosiloxane particles obtained by a method of such this invention are real ball-like monodisperse particles. A coefficient of variation (CV value) is calculated by a lower type.

$$CV \text{ value (\%)} = (\text{standard deviation} / \text{mean particle diameter of particle diameter}) \times 100$$
 [0040]

Next, a manufacturing method of a silica particle of this invention is explained. This method carries out baking treatment of the polyorganosiloxane particles, and decomposes an organic group contained in it, it is a method of manufacturing a silica particle and polyorganosiloxane particles obtained with the above-mentioned manufacturing method are used for it as the above-mentioned polyorganosiloxane particles.

[0041]It is beyond a temperature lower 100 ** than decomposition temperature of an organic group contained in it in this method in polyorganosiloxane particles obtained by an above-mentioned method, And after carrying out reserve baking treatment at temperature of the range of less than decomposition temperature of the organic group concerned, baking treatment is carried out at temperature more than decomposition temperature of the organic group concerned, and a silica particle is manufactured.

[0042]If temperature up is promptly carried out to temperature more than decomposition temperature of an organic group contained in these polyorganosiloxane particles and it calcinates, Decomposition of the organic group concerned and desorption take place rapidly,

depending on the case, disruptive strength of particles being unable to fall or bearing rapid contraction cannot be finished, and the situations which are not preferred -- particles can be broken -- may be invited. However, like this invention, after performing reserve baking treatment at temperature of the range of less than decomposition temperature of the organic group concerned, the situation which is not preferred as for the above is avoidable [it is beyond a temperature lower 100 ° than decomposition temperature of the organic group concerned, and] by carrying out baking treatment at temperature more than decomposition temperature of the organic group concerned. As for selection of firing time, when processing at a comparatively low temperature when it has the organic group for which it depends on a kind of organic group which constitutes polyorganosiloxane particles and which is easy to carry out a pyrolysis has an organic group which cannot carry out a pyrolysis easily desirably and on the contrary, processing at an elevated temperature is preferred. Anyway, what is necessary is just to select optimal conditions according to needed disruptive strength and elastic modulus. Specifically In the case of polymethylsilsesquioxane (PMSO) / polyvinyl silsesquioxane (PVSO) composite particle. After holding at temperature of the range of 300-500 ° for about 3 to 50 hours and performing reserve baking treatment, at temperature of the range of 600-1300 °, it holds for about 3 to 50 hours, baking treatment is carried out, and an organic group is decomposed thoroughly.

[0043]In order to carry out oxidative degradation of the organic group and to silica-ize it as an atmosphere in the above-mentioned baking treatment, it is preferred that an oxygen density is more than 10 capacity % more than fixed, for example. There is no restriction in particular about a baking apparatus, and publicly known baking apparatus, such as an electric furnace and a rotary kiln, can be used.

[0044]

[Example]Next, although an example explains this invention still in detail, this invention is not limited at all by these examples.

500 g of methyl trimetoxysilane (it is hereafter written as MTMS.) was added to the preparation ion exchange water 5000g of the liquid for example 1(1) seed particle formation, and it agitated at 100 rpm at 30 °. Although it was distributing in the state of the oil droplet in solution, about 3 hours afterward, it dissolved thoroughly, and MTMS became a homogeneous solution, and made this the liquid for seed particle formation at the beginning of MTMS addition.

[0045](2) MTMS3300g was added to the preparation ion exchange water 33000g of the liquid for particle diameter growth, and it agitated at 100 rpm at 30 °. Although it was distributing in the state of the oil droplet in solution, about 3 hours afterward, it dissolved thoroughly, and MTMS became a uniform solution, and made this the liquid for particle diameter growth at the beginning of MTMS addition.

[0046](3) In the liquid for seed particle formation prepared by the formation above (1) of seed

particles, the agitating speed was lowered to 30 rpm and 50 ml of 1-mol [l.] ammonia solutions were added at a stretch. 2 minutes after adding the ammonia solution, particles grew, and the solution became cloudy. The pH of the seed particle liquid 30 minutes after ammonia solution addition was 9.47.

[0047](4) 0.2 ml of seed particle liquid 30 minutes after [of ammonia solution addition of measurement of seed particle diameter, and the addition (dilution magnification) of the liquid for particle diameter growth] calculatively in an account (3), In addition to 2 ml of 0.1 mass % PVA solutions, particle diameter was promptly measured with the Coulter counter. As a result, seed particles were 2.784 micrometers (1.49% of CV value) in mean particle diameter. Formula (III) which develops the above-mentioned expression-of-relations (II) for the mean particle diameter and the purpose last particle diameter of the seed particles obtained by setting the purpose last particle diameter as 6.683 micrometers with the dilution magnification K

[0048]

[Equation 2]

$$\text{希釈倍率 } K = \frac{\{ (R^3 - r^3) / r^3 \} \times (m/M) - A}{B} \quad \dots \quad \text{(III)}$$

[0049](however, A and B are constants decided by the growth reaction conditions of seed particles, and it can ask by the method shown later in this example.) -- dilution magnification K10.80 time was obtained by substituting and calculating.

[0050](5) The seed particle liquid 3360g obtained above (3) so that it might become the dilution magnification 10.06 computed above (4) by this was added, agitating 36300 g of whole quantity of the liquid for particle diameter growth of the growth above (2) of particle diameter at 20 rpm.

[0051](6) Particle diameter was measured with an optical microscope video micrometer (the Olympus video micrometer "VM-50") every 10 minutes after addition of the seed particle liquid in the reaction stop above (5). 1 hour, and [1 hour and 10 minutes] after addition, particle diameter is all about 6.7 micrometers.

It judged that particle diameter growth was completed and riped at the room temperature for 16 hours by dropping the 25 mass % ammonia solution 500g with a metering pump.

[0052]Thus, the yield of the obtained particles was 83%, and when it measured particle diameter with the Coulter counter, it was 6.652 micrometers (1.57% of CV value) in mean particle diameter. As compared with the purpose last particle diameter which set up this particle diameter in the above (4), that difference is -0.031micrometer (0.46% of particle diameter error).

The particles very near the purpose particle diameter were obtained.

[0053]<Calculation of the constants A and B> 0.2 ml of seed particle liquid 30 minutes after [of ammonia solution addition] in the above (3), After measuring mean particle diameter with a Coulter counter promptly in addition to 2 ml of 0.1 mass % PVA solutions, this seed particle liquid was added in the liquid for particle growth of the above (2) under churning at 20 rpm. [0054]Subsequently, particle diameter was measured with said video micrometer every 10 minutes after addition of seed particle liquid, and after checking that the particle diameter growth after 1 hour and 10 minutes had stopped, the 25 mass % ammonia solution 500g was dropped with the metering pump. Next, after the centrifuge separated the obtained particles with water, mean particle diameter was measured after desiccation using methanol. The above-mentioned operation was performed 4 times so that the additions of seed particle liquid might differ. The result is shown in Table 1.

[0055]

[Table 1]

表 1

シード粒子の 平均粒子径 (μm)	シード粒子液 添加量 (g)	シード粒子成長 後の平均粒子径 (μm)	補正係数 [C]
3. 128	2420	8. 251	1. 16
2. 954	3102	7. 250	1. 18
2. 351	3800	5. 467	1. 21
2. 875	4818	6. 237	1. 22

[0056]Table 1 showed that the correction factor C and the addition of seed particle liquid followed the proportional expression $C = 0.000026 \times (\text{seed particle liquid addition}) + 1.101$. From a seed particle liquid addition, since the dilution magnification K is calculable, an upper type is set to $C = 0.942/K + 1.101$, and can be found with $A = 0.942$ and $B = 1.101$.

[0057]Putting 1 l. of aqueous ammonia solutions adjusted the pH to 9.6 into a reaction vessel with a comparative example 1(1) seed particle liquid preparation process agitating device, and agitating at 20 rpm, MTMS100g was added slowly and the MTMS layer was made to form in the upper layer. Subsequently, this was agitated until the upper layer disappeared thoroughly at 30 **, and seed particles were made to generate. Under the present circumstances, the pH of reaction mixture was 8.4. The time which making seed particles generate took was 4 hours. [0058]In order to measure the particle diameter of this seed particle, after having taken a little reaction mixture, adding the 25 mass % ammonia solution and riping, when the Coulter counter performed particle diameter measurement, the CV value was 3.1% in the mean particle diameter of 2.7 micrometers. Seed particle liquid was prepared by diluting the above-mentioned reaction mixture so that it may become one 20 times the dilution magnification of

this with pure water. pH in this case was 8.2.

[0059](2) Putting 20 l. of seed particle liquid prepared by the seed particle growth process above (1) into a reaction vessel with an agitating device, and agitating it at 20 rpm, MTMS 2000g was added slowly and the MTMS layer was made to form in the upper layer. After agitating until the upper layer disappears thoroughly at 30 **, 20 ml of 25 mass % ammonia solutions were added, and the reaction was terminated. The time which seed particle growth took was 18 hours. Thus, when the particle diameter of the obtained particles was measured, with the mean particle diameter of 7.4 micrometers, a CV value is 4.1%, coalescence-ization of seed particles and the particles under growth took place during the reaction, and the large particles of particle size distribution were obtained.

[0060]After drying the particles whose mean particle diameter after the seed particle growth obtained in example 2 Example 1 is 6.237 micrometers, on condition of for 2 l. of air flow rate/, Temperature up was carried out from a room temperature to 400 **, after holding for 24 hours and carrying out preliminary calcination at the temperature, temperature up was carried out to 600 **, at the temperature, it held for 9 hours and actual calcination was carried out. It cooled to the room temperature after this calcination, and calcination particles were taken out. When observed with the Coulter counter about this calcination particle, mean particle diameter was 5.488 micrometers and the CV value was 1.52%.

[0061]

[Effect of the Invention]According to the method of this invention, it is comparatively big particle diameter (about 4-10 micrometers), and yield is good in a short time, and, moreover, it is not restricted to the specific gravity of a raw material, but the polyorganosiloxane particles of mono dispersion [particle size distribution] can be manufactured so that the thing of desired particle diameter may be obtained. The polyorganosiloxane particles obtained by this method are preferred as the spacer for liquid crystal displays, standard particles, etc. By carrying out baking treatment of the polyorganosiloxane particles obtained with the described method on specific conditions according to the method of this invention, It has particle diameter suitable as the spacer for liquid crystal displays, standard particles, etc., and particle size distribution can manufacture a mono dispersion silica particle by simple operation highly in a short time.

[Translation done.]